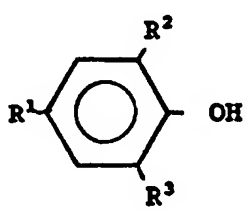




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/NL95/00242 (22) International Filing Date: 10 July 1995 (10.07.95) (30) Priority Data: 9400644 11 July 1994 (11.07.94) BE (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): OEVERING, Henk [NL/NL]; Burg. Eussenstraat 46, NL-6181 BR Stein (NL). WERUMEUS BUNING, Gerard, Hidde [NL/NL]; Past. Meulenbergsstraat 20, NL-6438 HZ Schinnen (NL). MEIJER, Egbert, Willem [NL/NL]; Schoenmakerslaan 7, NL-5583 GC Waalre (NL). VAN AERT, Hubertus, Adrianus, Maria [NL/NL]; Overbergseweg 9, NL-4635 RG Huybergen (NL). OUT, Gerardus, Jacobus, Joseph [NL/NL]; Wolkammersdreef 59c, NL-6216 RM Maastricht (NL). (74) Agent: SCHELTUS, Irma; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published With international search report. In English translation (filed in Dutch).
(54) Title: MULTIHYDROXY-FUNCTIONAL OLIGOPHENYLENE OXIDE <div style="text-align: center;">  <chem>Oc1cc(R1)cc(R2)c(R3)c1</chem> (I) </div> (57) Abstract <p>Multihydroxy-functional oligophenylene oxide obtainable by reacting a compound containing hydroxyaryl comprising at least three hydroxyaryl groups according to formula (I), wherein R¹ = an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms, R², R³ = H or an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms, or two of the R¹, R² or R³ groups together constitute a ring structure containing 4-50 carbon atoms with a polyphenylene oxide in the presence of a catalyst complex comprising a transition metal and and amine.</p>		

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MULTIHYDROXY-FUNCTIONAL OLIGOPHENYLENE OXIDE

5

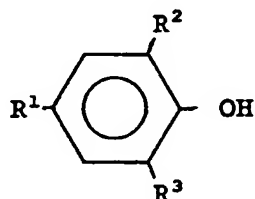
The invention relates to multihydroxy-functional oligophenylene oxide.

10 Mono- and dihydroxy-functional oligophenylene oxides are known from GB-A-1,119,914. This publication describes mono- and difunctional oligophenylene oxides that are prepared by a reaction between poly-(1,4-phenylene oxide) and a mono- or diphenol. This reaction is activated by the presence of an initiator, such as a peroxide or a catalyst
15 containing a copper compound.

The aim of the invention is the preparation of multihydroxy-functional oligophenylene oxides.

According to the invention these compounds are prepared by reacting a compound containing hydroxyaryl
20 comprising at least three hydroxyaryl groups according to the formula

25



where

30 R¹ = an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,
R², R³ = H or an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,
or two of the R¹, R² or R³ groups together constitute a
35 ring structure containing 4-50 carbon atoms, with a polyphenylene oxide in the presence of a catalyst complex containing a transition metal and an amine,

This results in the preparation of multihydroxy-functional oligophenylene oxide in a practically pure form.

The multihydroxy-functional oligophenylene oxide
5 has a high mechanical stability, in contrast with mono-
and dihydroxy-functional oligophenylene oxides.
The spherical multihydroxy-functional oligophenylene
oxides obtained by reaction of, for instance a calixarene
or a dendrimer with polyphenylene oxide are very suitable
10 for use as a fluidity improving agent in other polymers,
such as polyphenylene oxide and mixtures containing
polyphenylene oxide.

According to the invention, the reaction between
the compound containing hydroxyaryl and the polyphenylene
15 oxide is carried out in the presence of a catalyst complex
containing a transition metal and an amine.

As the amine, the catalyst complex may contain
aliphatic amines or compounds containing pyridine, such as
diethylamine, dibutylamine, tetramethylene diamine,
20 oligomeric amines, polyvinyl pyridine, pyridine and
dimethylaminopyridine.

Preferably the catalyst complex contains
dimethylaminopyridine.

The catalyst complex also contains a transition
25 metal. The transition metal is chosen from groups 8-11 of
the Periodic System of the Elements (Handbook of Chemistry
and Physics, 70th edition, CRC Press, 1989-1990).
Preferably the transition metal is chosen from the group
comprising copper, manganese, iron and cobalt.
30 With particular preference the catalyst complex contains
copper.

Examples of copper compounds which can be used
are copper(I) chloride, copper(I) acetate or copper(I)
carboxylate. The halides, acetates and carboxylates of
35 copper(II) may also be used.

During the reaction of the polyphenylene oxide

with the compound containing hydroxyaryl a transesterification takes place, in which a hydroxyl-functional oligophenylene oxide is formed.

'Transesterification' is understood to mean: the
5 redistribution of the phenol monomers constituting the polyphenylene oxide among the hydroxyaryl groups of the compound containing hydroxyaryl so that oligophenylene oxides with the same number-average molecular weight are formed. An oligophenylene oxide is formed as an 'arm' onto
10 the compound containing hydroxyaryl.

'Oligophenylene oxide' is understood to mean an oligomer of phenol monomers containing at least one chain of monomers that comprises between 2 and 70 monomer units.

An advantage of the process for the preparation
15 of the multihydroxy-functional oligophenylene oxides described above is that by this process the multihydroxy-functional oligophenylene oxides are obtained in a practically pure form in a simple way.

In principle, all compounds containing
20 hydroxyaryl can be used as the compounds containing hydroxyaryl comprising at least three hydroxyaryl groups as defined by the above formula.

Examples of compounds containing hydroxyaryl comprising at least three hydroxyaryl groups are: star-shaped phenols,
25 phenolic resins and other phenol-modified polymers, calix-(n)arenes and dendrimers containing terminal hydroxyaryl groups.

Examples of star-shaped phenols are: 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-tertiary-butylphenol,
30 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-octylphenol, 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-isooctylphenol, 2,6-bis-(4'-hydroxy-3',5'-dimethylbenzyl)-4-isopropylphenol, 2,4,6-tri-(4'-hydroxy-3',5'-dimethylbenzyl)phenol, (3,3',5,5'-tetra(4"-hydroxybenzyl)-
35 4,4'-dihydroxyphenyl)methane, (3,3',5,5'-tetra(4"-hydroxy-3",5"-dimethylbenzyl)-4,4'-dihydroxydiphenyl)methane, 2,2-

- (3,3',5,5'-tetra(4"-hydroxy-3",5"-dimethylbenzyl)-4,4'-
dihydroxydiphenyl)propane, 1,1-(3,3',5,5'-tetra(4"-
hydroxy-3",5"-dimethylbenzyl)-4,4'-
dihydroxydiphenyl)cyclohexane, 1,1,4,4-tetra(4-
5 hydroxyphenyl)cyclohexane and 1,1,4,4-tetra(3,5-dimethyl-
4-hydroxyphenyl)cyclohexane.

Resols and novolaks can be mentioned as phenolic resins.

Examples of other phenol-modified polymers are:

- 10 poly(p-hydroxystyrene), copolymers of p-hydroxystyrene and
other monomers, terminal-hydroxyaryl-containing
polycarbonate, polyetherimide and polysulphone.
Calixarenes are metacyclophanes with a hydroxyl group at
each 2 position. They are prepared via a base-catalysed
15 condensation reaction of a p-alkylphenol and formaldehyde.
They are for example described in 'Calixarenes, C.D.
Gutsche, The Royal Society of Chemistry, Cambridge
(1989)".
Tertiary-butylcalix(4)arene, tertiary-butylcalix(6)arene
20 and tertiary-butylcalix(8)arene can for example be
mentioned as calixarenes.

- Dendrimers are three-dimensional, highly
branched oligomeric and polymeric molecules with an
exactly defined chemical structure. Dendrimers are
25 generally composed of a core, a number of generations of
branches and an external surface.

- The generations of branches are composed of structural
units repeating themselves, which are radially bound to
the core. The external surface is composed of the
30 functional groups of the last generation. Examples of
suitable dendrimers are for example described in Angew.
Chem. Int. Ed. Engl. 29 (1990), pp. 138-175 and
PCT/NL93/00008. As the functional groups in the external
surface, the dendrimers that can be used according to the
35 invention contain the hydroxyaryl groups according to the
above formula. Examples of these dendrimers are: 4-

cascade: 1,4-diaminobutane[4]:N-T-BOC-L-tyrosine-propylamide, 8-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)⁴:N-T-BOC-L-tyrosine-propylamide), 16-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)¹²:N-T-BOC-L-tyrosine-propylamide), 32-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)²⁸:N-T-BOC-L-tyrosine-propylamide) and 64-cascade: 1,4-diaminobutane[4]: (1-azabutyridene)⁶⁰:N-T-BOC-L-tyrosine-propylamide).

As polyphenylene oxide use can be made of all the known polyphenylene oxides, as for example described in 'Encyclopedia of polymer science and engineering, Vol. 13, John Wiley & Sons, Inc. (1988), pp 1-30'.

Hydroxyl-functional oligophenylene oxides can be used in a wide field of applications. The spherical multihydroxyl-functional oligophenylene oxides can for example be used as fluidity improving agents in other polymers. Also conceivable is a mixture of polyphenylene oxide and (a) multifunctional oligophenylene oxide(s) that makes the polyphenylene oxide better processable.

The multi-hydroxy-functional oligophenylene oxides can also be used as fluidity improving agents in mixtures of polyphenylene oxide with other polymers, such as polystyrene, polyamide-6,6 and polypropylene. Spherical multihydroxy-functional oligophenylene oxides are better mixable with other polymers than polyphenylene oxide. The oligophenylene oxides also possess a high chemical resistance.

To improve the mechanical properties of polymers they can be polymerised in thermosets, such as epoxy resin, (meth)acrylates, polyesters and silicones. Further multihydroxy-functional oligophenylene oxides improve the flame-retardant properties of thermosets.

The invention will be further illustrated with reference to the examples without being limited hereto.

Examples

The materials and methods used:

- low-molecular-weight PPO: a PPO with an M_n of 3800, $D = 2.5$;
- 5 - Cu(I)Cl , analytical reagent, from Merck;
- dimethylaminopyridine (DMAP): 99% DMAP from Janssen Chimica;
- the number-average molecular weight, M_n , was determined via $^1\text{H-NMR}$ using a Bruker AM-400
- 10 spectrometer.

Example I

5.003 g of PPO-OH ($M_n = 8200$) and 0.6717 g of tertiary-butylcalix(8)arene were together dissolved in 250
15 ml of chloroform. 0.0475 g of CuCl and 0.0974 g of DMAP were added as the catalyst. A 20:80 mixture of oxygen:nitrogen was bubbled through at 20 ml/min. The reaction was carried out for 40 hours at room temperature. The product was shaken out using a 10% EDTA solution. The
20 product was precipitated from the chloroform phase using heptane.

The number-average molecular weight of the oligophenylene oxide formed was 11590. The average length of the oligophenylene oxide chains was $n = 10.7$.

25

Example II

4.0 g of 2,6-bis(4'-hydroxy-3',5'-dimethylbenzyl)-4-isooctylphenol and 15.4 g of low-molecular-weight PPO were dissolved in 200 ml of
30 chloroform. Then 0.12 g of CuCl and 0.24 g of DMAP in 50 ml of chloroform were added. After 5 hours' reaction under nitrogen, compressed air was passed over the mixture for 1.5 hours. After another 20 hours' reaction under nitrogen, compressed air was bubbled through for 2 hours.
35 Then the reaction was continued for another 23 hours under nitrogen. Then the product was separated from the reaction

mixture, washed using a 10% HCl solution and dried. The number-average molecular weight of the oligophenylene oxide formed was 2764. The average length of the oligophenylene oxide chains was $n = 5$.

5

Example III

5.0 g of 2,6-bis(4'-hydroxy-3',5'-dimethylbenzyl)-4-isooctylphenol and 7.7 g of low-molecular-weight PPO were dissolved in 200 ml of chloroform. Then 0.11 g of CuCl and 0.25 g of DMAP in 50 ml of chloroform were added. After 24 hours' reaction under nitrogen, oxygen was passed over the solution for 15 minutes. Then 5.0 g of pyridine was added, after which the reaction was continued under nitrogen. After a total of 72 hours' reaction the product was separated from the reaction mixture, washed using a 10% HCl solution and dried. The number-average molecular weight of the oligophenylene oxide formed was 1102. The average length of the oligophenylene oxide chains was $n = 2$.

20

Example IV

Synthesis of a multihydroxy-functional oligophenylene oxide with $n = 4$

0.209 g PPO-OH ($M_n = 2833$) and 0.0521 g poly(p-hydroxystyrene) ($M_w = 30.000$) were dissolved in 10 ml tetrahydrofuran (THF), 2.5 mg CuCl and 5 mg DMAP were added as the catalyst.

After 3 days reaction under air heptane was added, causing the product obtained to precipitate.

30 In the same way as described above, but with other ratio's of PPO-OH versus poly-(p-hydroxystyrene) multihydroxy-functional oligophenylene oxides were prepared with $n = 1$ and $n = 20$.

TABLE 1:

n	M _n
1	3130
4	4200
20	8370

Example VSynthesis of a multihydroxy-functional oligophenylene oxide with n = 4

- 10 5 g PP (Vestoran®, see table) and 1.41 g (2.3 mmol) 1,1,4,4-tetrakis(4-hydroxy-3,5-dimethylphenyl)cyclohexane (1) were dissolved in 60 ml boiling THF.
- 0.02 g CuCl and 0.042 g DMAP were added as the catalyst.
- 15 After the reaction mixture was refluxed for 24 hours 25 ml 10% HCl was added during stirring.
- The suspension formed was extracted 3 times with chloroform. The collected organic phases were washed with a saturated NaCl-solution, dried over Na₂SO₄ and reduced by
- 20 evaporation. 5.58 g (87%) product was obtained.
- The amounts of (1), CuCl and DMAP were varied for the synthesis of the other polymers.
- The polymers obtained were characterised with ¹H-NMR and gelpermeation chromatography combined with a viscosity
- 25 detector.

TABLE 2:

oligomer n	M_n (g/mol)	M_w (g/mol) ^{a)}	$[\eta]$ (dl/g) ^{b)}
armlength 4	864	4800	0,130
armlength 8	2028	15500	0,245
armlength 16	3492	18700	0,285
armlength 32	5076	23000	0,319
armlength 64	7518	33800	0,387
Vestoran® -	9360	36800	0,472

- 10 a) the molecular weight was determined with
gelpermeation chromatography according to ASTM-D
3593-80
- b) the viscosity of each fraction was determined with a
viscosity detector after gelpermeation chromatography
15 was performed. This method is described in 'Journal
of Liquid Chromatography' (1990); Yau W.W. & Rementer
S.W.; Vol. 13, page 627.
- The Zimm-Stockmayer theory teaches that the value of
the ratio between $[\eta]_{\text{star}}/[\eta]_{\text{lin}}$ indicates the degree
20 of branching.
- $[\eta]_{\text{star}}$ and $[\eta]_{\text{lin}}$ must be determined on star-shaped
and linear polymers with comparable molecular weight.
Calculations of $g' = [\eta]_{\text{star}}/[\eta]_{\text{lin}}$ show that the
oligomers with armlength 8, 16, 32 and 64 have a
25 degree of branching of 4.
- The calculations were performed in the way that is
described in "Zimm, B.H. and Stockmayer, W.M.;
Journal of Chemistry & Physics (1949), Vol. 17, p.
1301", "Zimm, B.H. and Kilb R.W.; Journal of Polymer
30 Science (1959), Vol. 37, p. 19" and Roovers J. et
all; Macromolecules (1993), Vol. 26, p. 4324.

Examples VI-XIUsed Dendrimers:

- 4-cascade: 1,4-diaminobutane[4] : N-T-BOC-L-tyrosinepropylamide = DAB(PA)₄-tyrosine
- 8-cascade: 1,4-diaminobutane[4] : (1-azabutylidene)⁴ : N-T-BOC-L-tyrosinepropylamide) = DAB(PA)₈-tyrosine
- 32-cascade: 1,4-diaminobutane[4] : (1-azabutylidene)²⁸ : N-T-BOC-L-tyrosinepropylamide) = DAB(PA)₃₂-tyrosine
- 10 - 64-cascade: 1,4-diaminobutane[4] : (1-azabutylidene)⁶⁰ " N-T-BOC-L-tyrosine) and modifications hereof with less than 100% L-tyrosine-endgroups.

Example VI

- 15 0.150 g DAB(PA)₈-tyrosine in 2 ml dimethylsulfoxide (DMSO) was slowly added to a solution of 1.14 g PPO (Mn= 5520) in 30 ml chloroform in an argon atmosphere.
- 11.5 mg CuCl and 25.4 mg DMAP were added as a catalyst.
- 20 The solution was stirred for 4 weeks under argon. The product was obtained after shaking the solution with a 10% EDTA solution and a 10% HCl-solution, whereafter the solution was reduced by evaporation until 15 ml was left and was added to 200 ml methanol.

25

Examples VII-VIII

Example VI was repeated with DAB(PA)₃₂-tyrosine and DAB(PA)₆₄-tyrosine instead of DAB(PA)₈-tyrosine.

30 Example IX

Example VI was repeated with 0.12 g DAB(PA)₆₄ (80% L-tyrosine; 20% d-phenylalanine) and 0.18 g PPO. 2.5 mg CuCl and 5.2 mg DMAP were added as the catalyst. Chloroform was used as a solvent for the dendrimer.

35

Example X

Example IX was repeated with 0.32 g DAB(PA)₆₄ (50% L-tyrosine; 50% d-phenylalanine) and 1.16 g PPO. 9.7 mg CuCl and 19.5 mg DMAP were added as the catalyst.

5

Example XI

Example IX was repeated with 0.12 g DAB(PA)₆₄ (20% L-tyrosine; 80% d-phenylalanine) and 0.33 g PPO. 3.5 mg CuCl and 6.7 mg DMAP were added as the catalyst.

10

TABLE 3:

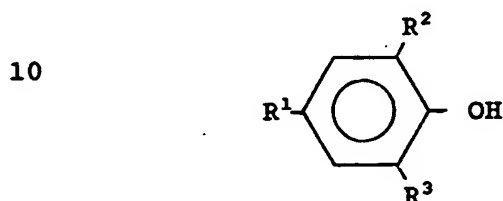
Example	Arms on dendrimer	% L-tyrosine	n	% PPO-arms in product
VI	8	100	22.5	8
VII	32	100	22.5	32
VIII	64	100	22.5	64
IX	64	80	22.5	51.2
X	64	50	22.5	32
XI	64	20	22.5	12.8

15

20

C L A I M S

1. Multihydroxy-functional oligophenylene oxide
5 obtainable by reacting a compound containing hydroxyaryl comprising at least three hydroxyaryl groups according to the formula



- 15 where
R¹ = an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,
R², R³ = H or an aromatic, aliphatic or cycloaliphatic group containing 1-50 carbon atoms,
20 or two of the R¹, R² or R³ groups together constitute a ring structure containing 4-50 carbon atoms with a polyphenylene oxide in the presence of a catalyst complex comprising a transition metal and an amine.
- 25 2. Multi-hydroxy functional oligophenylene oxide according to claim 1, characterised in that the compound containing hydroxyaryl is a star-shaped phenol.
- 30 3. Multihydroxy-functional oligophenylene oxide according to claim 1, characterized in that the compound containing hydroxyaryl is a dendrimer containing terminal hydroxyaryl groups as defined in claim 1.
- 35 4. Mixture of a polyphenylene oxide and a multihydroxy-functional oligophenylene oxide according to any one of claims 1-3.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/NL 95/00242

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G65/48 C07C43/23 C07C41/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,1 119 914 (GENERAL ELECTRIC) 17 July 1968 see page 2, line 4 - page 5, line 45 ---	1-4
A	AM. CHEM. SOC. DIV. POLYMERS CHEM. PREPRINTS, vol.7, no.1, 1966 pages 166 - 172 G. D. COOPER ET AL 'The redistribution of hydroxyarylene ethers' see page 168 - page 169 ---	1-4
A	NL,A,6 803 930 (GENERAL ELECTRIC) 23 September 1968 see examples XXIX,XXX --- -/--	1-4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

29 September 1995

Date of mailing of the international search report

- 6. 10. 95

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INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/NL 95/00242

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF ORGANIC CHEMISTRY., vol.34, no.2, February 1969, EASTON US pages 297 - 303 D. M. WHITE 'The synthesis of 4-hydroxyarylene ethers by the equilibration of phenols with poly(2,6-dimethyl-1,4-phenylene ether)' see page 297; document cited in the application ---	1-4
A	EP,A,0 550 209 (GENERAL ELECTRIC) 7 July 1993 see the claims; document cited in the application ---	1-4
A	EP,A,0 215 257 (BAYER) 25 March 1987 see the claims; document cited in the application -----	1-4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 95/00242

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		US-A- 3496236	17-02-70
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		FR-A- 1566600	09-05-69
		GB-A- 1202096	12-08-70
		US-A- 3392147	09-07-68

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		JP-A- 62039628	20-02-87
